BaCoO2+δ

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$BaCoO_{2+\delta}$: A new highly oxygen deficient perovskite-related phase with unusual Co coordination obtained by high temperature reaction with short reaction times

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A new highly oxygen deficient metastable modification of perovskite-related $BaCoO_{2+\delta}$ (δ ~ 0.01 – 0.02) has been prepared using high temperature reactions with short heating times. This defect rich compound has at least partially square planar coordination of the Co^{2+} ions, a highly unusual coordination environment for Co. Low temperature neutron powder diffraction showed a G-type antiferromagnetic ordering, confirmed by SQUID magnetic measurements, which indicate a high Néel temperature of 220 K. This work shows how novel defective phases can be synthesized by exploiting short reaction times in solid state synthesis, thus offering an alternative route for new materials synthesis.

Perovskite-type or perovskite-related ABX_{3-y} compounds are interesting candidates for a wide range of applications in the field of electronics [1], solid oxide fuel [2] and solar cells [3]. In particular, cobalt based perovskites $ACoO_{3-y}$ have drawn a lot of attention due to their interesting electronic, magnetic and catalytic properties [4, 5]. For the latter, especially such compounds with a Co-sublattice, which can be derived from the cubic aristotype structure (i. e. from a close cubic packed (*ccp)* arrangement of AX_3 layers with Co occupying ¼ of octahedral voids), were reported to be of most interest. Within such an atomic arrangement, the structure is highly flexible and can tolerate large amounts of anion vacancies, ABX_{3-y} [6-8] , with values of y up to 1 being known, from which a high mobility of oxygen ions originates.

For non-stoichiometric $BaCoO_{3-y}$ perovskite-related oxides, a broad structural variety of compounds has been found depending on the detailed value of y. Those were summarized by Raveau et al.[5] as well as by Mentré et al.[9] with hexagonal modifications known for oxygen rich systems (2H, 5H, 12H). For large values of y, the most oxygen deficient cubic perovskite phase $BaCoO_{2.22}$[9] as well as trigonal $BaCoO_2$ [10] are known, where the structure of the latter was reported as an ordering variant ($P3_121$) of the cubic aristotype structure with only tetrahedral coordination of the Co ions.

Apart from the thermodynamically stable modifications, highly anion deficient metastable compounds have been previously prepared almost entirely via hydride based reductions [7, 8]. Such reactions are time consuming multi step procedures which require additional washing steps to obtain a phase pure sample. In contrast, direct synthesis of such metastable ABO_2 type perovskite-related phases has not been reported so far.

In this article, we report for the first time the preparation of a highly oxygen deficient tetragonal modification of $BaCoO_{2+\delta}$ synthesized using a simple route, involving high temperature solid state synthesis with considerably short reaction times (twice at 1000 °C for 1 h using heating / cooling rates of 2 °C/min) of high energy ball milled powders of $BaCO_3$ and Co_3O_4 under pure argon atmosphere. The synthesis conditions show a very narrow sweet spot. Changing the conditions slightly (temperature, flow of argon, heating time, etc.) results either in the formation of the trigonal $BaCoO_2$ modification, or cubic $BaCoO_{2.22}$, or melting of the sample.

The composition of the sample was determined from a combination of iodometric titration and energy dispersive X-ray spectroscopy (EDAX, Figure S1 in ESI) [9, 11]. The average oxidation state of Co was determined to be $Co^{+2.03(2)}$ with a 1:1 ratio of Ba:Co. This results in an overall composition of the sample close to $BaCoO_{2+\delta}$ with δ ~ 0.01 – 0.02. Since carbonate has been previously reported to be stabilized on the B site within the

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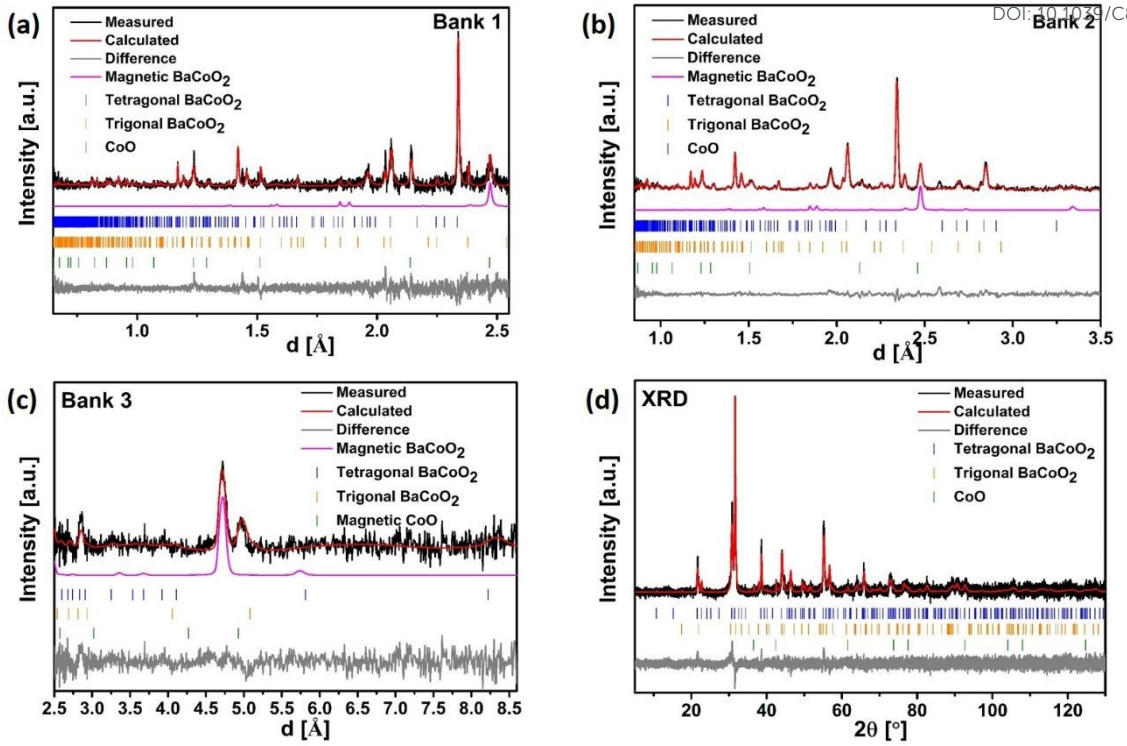

Figure 1: Coupled Rietveld refinement of the neutron diffraction data recorded at 10 K and room temperature X-ray diffraction patterns of $BaCoO_{2+\delta}$ using model#1 (see text).

perovskite structure, the presence of this species was further ruled out by the use of Raman spectroscopy [12] (Figure S2 in ESI). The structure and phase composition of the obtained powder was studied via a combined Rietveld analysis of X-ray and neutron powder diffraction data. All of the reflections could be indexed with a 2 x 2 x 1 tetragonally distorted superstructure of the cubic perovskite aristotype (Figure 1) with a = 8.2201(15) Å and c = 3.9181(7) Å, additionally, 8.8(3) wt-% of trigonal $BaCoO_2$ and ~ 3.1(3) wt-% of CoO were identified as impurity phases. Among the maximum subgroups of *Pm*-3*m* with those lattice parameter restrictions, only *P4/mmm* (and its *translationengleiche* subgroups, Figure S3 and S4 in ESI for structural relationship), allow for the (1 0 0) superstructure reflection observed at 10.74 °(2θ) (Figure S5 in ESI) in the XRD pattern.

This tetragonal distortion is unusual, since it implies a c/a ratio smaller than 0.5 (c_{prim}/a_{prim} < 1), which is often found for compounds with (partial) square planar coordination of the transition metal. Remarkably, only $Ba_{0.8}Sr_{0.2}FeO_2$ was previously reported to crystallize in such a 2 x 2 x 1 primitive superstructure by Kageyama et al. [6], with the B-site cation being located at three independent crystallographic sites (Ba @ 4*k*; Co @ 1*a*, 1*c*, 2*f*). For this compound, square planar, but also 6-fold coordination of Fe^{2+} and coordination numbers lower than four would have to result from the structural model suggested, originating from an only partial ordering of the anion vacancies, confirmed by Mössbauer spectroscopy. A structural similarity between the phase prepared here to this Fe-based phase is chemically plausible regarding the overall anion content and because barium ferrates / cobaltates are known for their structural similarity [11,13]. However, no tetrahedral coordination is possible from the ideal site symmetries of the Co sites (2x 4/*mmm*, 1x *mmm*). This is surprising with respect to the tetrahedral coordination found for the previously known modification of $BaCoO_2$ [10].

Therefore, we also investigated a second structural setting within the same space group, which differs by distribution of the Ba and Co ion on the different crystallographic sites (Ba @ 1*a*, 1*c*, 2*f*; Co @ 4*k*). In this structural setting, a tetrahedral coordination of Co is allowed from its site symmetry (*m*2*m*).

Both, the model suggested by Kageyama et al. [6] (model#1) as well as the alternative model (model#2) were used for the analysis of the neutron (ambient and 10 K) and X-ray diffraction data (see Table S1 and S4 for the starting and Table S2 and S5 for the refined structural models). Both models result in a good description of the diffraction data, with model#1 resulting in the best goodness of fit / R_{wp} values. Remarkably, no full ordering of oxygen vacancies was found for both models, and this implies that at least some of the Co^{2+} ions must be present in a square planar coordination or in a coordination with even lower coordination numbers (Figure 2a and b).

Subsequently, we attempted to refine the structure within the tetragonal *translationengleiche* subgroups of *P4/mmm*, which allow for further tilting of the polyhedra. However, such models do not result in a significant improvement of fit with respect to the additional parameters and do not result in an increase of localization of the oxygen ions and anion vacancies. Furthermore, model#2 does not become favourable over model#1. We also would like to emphasize, that the data showed no indication for further symmetry lowering, e. g. from

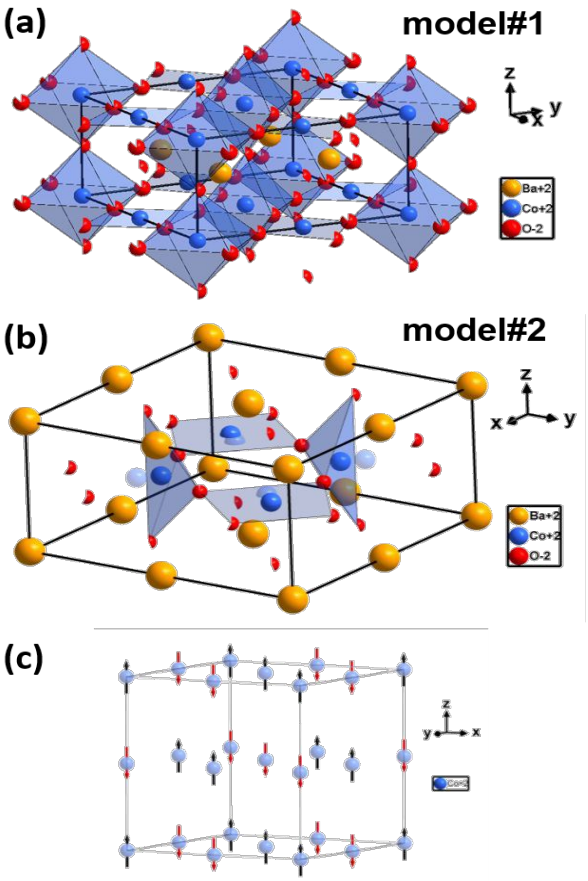

Figure 2: Structural representation of $BaCoO_{2+\delta}$: (a) model#1, (b) model#2. Oxygen sites are depicted to indicate their fractional occupancy. For model#2, a split site model was used to refine the position of the Co ion, and most plausible polyhedra are indicated for the different possible coordination scenarios. (c) G-type AFM structure found for the magnetic moments ($c_{magnetic}$ = 2 x $c_{nuclear}$).

the appearance of superstructure reflections or splitting of the reflections, and using structures within lower symmetry crystal systems did not result in an improved fit.

To the best of our knowledge, a planar coordination of Co^{2+} has not been observed so far in anion deficient perovskite structures [9], although it can be found, e. g., in $Sr_2CoO_2Cu_2S_2$ [14].

To obtain a deeper understanding on the role of coordination geometry around Co on the stability of a phase with ideal composition $BaCoO_2$, we carried out DFT based calculations on fully ordered models #1 and #2, with square planar and tetrahedral coordination of the Co ions, respectively, as well as on the trigonal modification (model #3). The values are summarized in Table S6, showing model #1 to be the least favourable setting and the trigonal modification to be energetically most favourable (E(#3) < E(#2) < E(#1), with differences of Δ(E(#3)-E(#1)) ~ -0.5 eV and Δ(E(#3)-E(#2)) ~ -0.25 eV). Therefore, the disorder generated by the small amount of additional oxygen δ (which are too costly to be calculated) must influence the overall structural stability, making the disordered tetragonal modification more favourable.

A magnetic phase transition was found to occur at a temperature of approximately 220 K, indicating antiferromagnetic (AFM) ordering (see Figure 3a; the magnetic properties are unknown for the trigonal phase of $BaCoO_2$; CoO

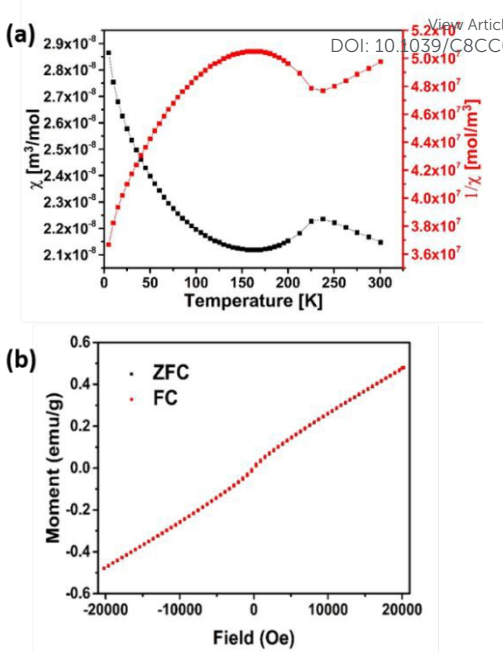

Figure 3: (a) Susceptibility vs temperature curve (black) and inverse susceptibility curve (red) for $BaCoO_{2+\delta}$ measured at the field of 2 Tesla.(b) M vs H curve for $BaCoO_2$ measured at 5 K.

orders AFM below ~ 290 K [9,15]). This is also in agreement with the presence of only a small residual ferromagnetic moment in the magnetisation curve recorded at 5 K (Figure 3b). To determine the magnetic structure of $BaCoO_{2+\delta}$, neutron diffraction data at 10 K were recorded. At this temperature, additional reflections appear as compared to the room temperature data. A part of them arise from the AFM ordering of CoO, and can be described with the magnetic structure of this phase as described previously [15]. The other reflections originate from the magnetic ordering of $BaCoO_{2+\delta}$ and can be indexed based on a magnetic *k*-vector of [0 0 ½]. We tested all models within the maximum magnetic subgroups of *P4/mmm*, and found that the magnetic scattering can be best described by the presence of anti-ferromagnetic (AFM) G-type order with the magnetic moment of 2.55(2) μ_B being aligned along the c-axis. This ordering corresponds to the magnetic symmetries P_c4/mcc (124.360) for model#1 or P_c4_2/mmc (131.444) for model#2 respectively, see Figure 2c. The refined magnetic moment is in agreement with what would be expected for high-spin Co^{2+} (3.7 μ_B), taking into account that the magnetic moment obtained from neutron diffraction is reduced by covalent contributions.

We also studied the conductivity of the sample by means of electrochemical impedance spectroscopy (Figure 4). The conductivity is of the order 10^{-8} S cm^{-1} at 298 K, which is significantly lower by ~ 3-4 orders of magnitude as compared to, e. g., $BaCoO_{1.80}(OH)_{0.86}$ with Co in a mixed valent +2/+3 oxidation state. The slope of the Arrhenius plot corresponds to an activation energy of 0.30(1) eV, and no blocking behaviour could be observed at low frequencies. Both suggest mainly electronic conductivity of the sample. The relatively low conductivity can be understood from the presence of mainly divalent Co^{2+}, and the similarity of activation energy to mixed valent $BaCoO_{1.80}(OH)_{0.86}$ [11] indicates a similar conduction

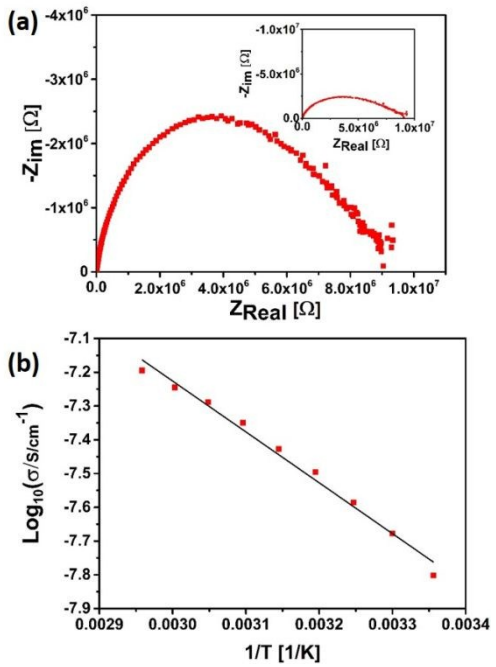

Figure 4: (a) Nyquist and (b) Arrhenius plot for temperature dependent total electrical conductivity of $BaCoO_{2+\delta}$ sample.

mechanism by electron hopping due to the presence of Co^{3+}.

We also found that the sample is highly sensitive towards re-oxidation by means of simultaneous thermal analysis (STA) (Figure S6 in ESI) in pure oxygen. The onset of mass increase due to oxygen uptake upon heating at ~425 K is in agreement with the exothermic peak in the DSC profile which is due to the oxygen uptake forming a compound of composition of $BaCoO_{2.40}$ at this point. XRD measurements showed that the sample is then composed of a cubic perovskite phase (as reported, e. g., for $BaCoO_{2.22}$ [9]) plus a further unknown phase. This is similar to what was observed previously for the dehydration of $BaCoO_{1.80}(OH)_{0.86}$ [11]. On further heating, the mass increase continues up to a temperature of approximately 900 K leading to formation of $BaCoO_{2.66(2)}$, and this oxygen uptake is then accompanied by a complete structural transformation to the 2H modification, see Figure S7 in ESI.

Conclusions

In summary, a new highly oxygen deficient metastable perovskite-related phase of barium cobaltate with composition of $BaCoO_{2+\delta}$ (δ ~ 0.01 -0.02) is reported in this article. The compound was found to show strong structural similarity to the previously reported Fe based system $Ba_{0.8}Sr_{0.2}FeO_2$ [6], with unusual coordination for Co^{2+} (which is at least partially square planar) and G-type AFM ordering below 220 K.

It is surprising that such a highly oxygen deficient metastable phase could be formed, although the structure of the thermodynamically most stable modification of $BaCoO_2$ can also be derived from the cubic perovskite structure (i. e., shows a nearly identical Ba/Co sublattice). Therefore, the incorporation of small amounts of additional oxygen δ via short reaction times and fine-tuned Ar gas flow, in combination with the milling-based activation of the precursors powders, are likely to be key to its formation. Thus, the findings presented here highlight the potential impact of small deviations of anion composition on anion ordering within a given cation lattice, and show how control of synthesis parameters can be exploited to produce new defective phases, thus offering an additional avenue for chemists to exploit in the quest for new materials.

Conflicts of interest

There are no conflicts to declare.

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A pinch of oxygen: Incorporation of small additional oxygen introduces partly square planar coordination into $BaCoO_{2+\delta}$.

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